maintenance of a vacuum. Vacuum pumps are, in general, not amenable to miniaturization, since they must possess the physical means to transport molecules from inside the system to the outside environment. The only restriction is the insistence on maintaining vacuum, with the assumption that many samples will be analysed by the same mass spectrometer. If a miniaturized mass spectrometer has a total evacuated volume of 1 mL (not outside the reasonable scale), then a vacuum reservoir of 100 mL suffices for pumping by virtue of expansion. Essentially the vacuum is a rechargeable resource. Removing of the vacuum hardware as a physical limitation to the size of the mass spectrometer will be a genuine innovation in the field. Hopefully, this same overview written ten years from now will document the applications of new miniaturized chromatography–mass spectrometry systems.

See Colour Plate 12.

Further Reading

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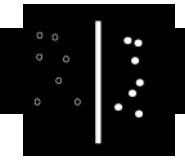
MEMBRANE SEPARATION



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Introduction

Since the 1970s industrial membrane separation technology has developed into a US$1–2 billion per year business. The market is fragmented, but can be divided into six principal industrial process areas: microfiltration, ultrafiltration, reverse osmosis, electrodialysis, gas separation and pervaporation. Dialysis, another membrane separation technique, is limited to two biomedical processes, haemodialysis (artificial kidneys) and blood oxygenators (artificial lungs). The market for these two biomedical applications is another US$2 $\times 10^9$ per year. Further membrane separation applications, including membrane contactors, membrane reactors and coupled and facilitated transport, are under development. Although similar membranes and membrane module designs are used in all of these process areas, the ways by which the separations are performed and the process applications are very different. A brief overview of each process is given here; more detailed descriptions of the individual processes are given elsewhere in the encyclopedia.

History

The concept of the ideal semipermeable membrane able to separate two species with the theoretical minimum work has been used by thermodynamicists for more than 150 years, but attempts to use membranes for practical separations did not begin until the 1900s, when Bechhold devised a technique for preparing nitrocellulose membranes of graded pore size. Later workers, particularly Zsigmondy, Bachmann, Elford and Ferry, refined these preparative techniques and membranes were used to separate a variety of laboratory solutions by dialysis and microfiltration.

By the 1930s, microporous membranes were produced commercially on a small scale. The first ion exchange membranes were made at about the same time; these were used by Teorell, Meyer and Seivers to develop their theory of ion transport. This work led eventually to the development of electrodialysis.

By the 1960s, therefore, the elements of modern membrane science had been developed, but membranes were only used in laboratories and in a few small, specialized industrial applications. There was no significant membrane industry, and total sales for all applications probably did not exceed US$10 million. Membrane processes suffered from three problems that prohibited their widespread use: they were too slow, too expensive and too unselective. Partial solutions to each of these problems have since been developed, and sales of membranes and membrane separation equipment have grown several hundred-fold. Currently, several tens of millions of square metres of membranes are produced each year, and a membrane industry has been created.

The problem of slow permeation rates through membranes was largely overcome in the late 1960s and early 1970s by the development of imperfection-free ultrathin membranes. These membranes are anisotropic structures and consist of a thin selective surface film supported by a much thicker microporous substrate to provide mechanical strength. Because the selective surface film is very thin, these membranes have high fluxes.

The problem of packing a large membrane area into a low-cost module has also been solved since the 1980s. The earliest module designs were plate-and-frame or tubular units similar to conventional heat exchangers. These designs are still used in some processes, such as ultrafiltration, in which the ability to clean fouling deposits from the membrane surface is important. However, the cost of both designs is relatively high, and in most processes they have been displaced by capillary, hollow-fine-fibre and spiral-wound module designs.

The problem of low selectivity remains one of the principal limitations of membrane processes. No general solution has been found, although substantial improvements have been made since the 1950s.

Ultrathin Membranes

The first useful ultrathin membranes were cellulose acetate reverse osmosis membranes produced by Loeb and Sourirajan, two researchers at the University of California at Los Angeles. The development of these thin, and hence high flux, membranes led to the reverse osmosis industry in the 1960s. In the Loeb–Sourirajan technique, a solution containing approximately 20% polymer is cast as a thin film on a nonwoven fabric web and is then precipitated by immersion in a bath of water. The water very rapidly precipitates the top surface of the cast film, forming the selective skin. This skin then slows down the entry of water into the underlying polymer solution, which precipitates much more slowly, forming a more porous substructure. A scanning electron micrograph showing the porous substructure and the selective skin of a Loeb–Sourirajan membrane is shown in **Figure 1**. The selective layer thickness is typically less than 0.2 μm.

About one-third of the reverse osmosis and almost all ultrafiltration membranes currently produced are made by the Loeb–Sourirajan technique. This type of membrane is also widely used in gas separation processes.

In recent years, new approaches have been developed to produce anisotropic membranes with even thinner selective layers than those made by the Loeb–Sourirajan method. Selective layers only a few tens of nanometers in thickness, and effectively free of imperfections, have been claimed for these so-called thin-film composite membranes. Thin-film composite membranes can be made by a number of methods, of which two are particularly important: coating with a dilute polymer solution and interfacial polymerization. In the coating method, which was developed first, a very dilute solution of the polymer is prepared in a volatile solvent, such as hexane. A thin film of this polymer solution is deposited on the microporous support surface by immersing and then slowly withdrawing the support from the solution. As the solvent evaporates, an extremely thin polymer film is left behind. This technique is used to manufacture ultrathin membranes for gas separation and pervaporation.

The second important method for preparing composite membranes is interfacial polymerization. In this method, an aqueous solution of a reactive monomer, such as a diamine, is deposited in the pores of a microporous support membrane. The membrane is then immersed in a water-immiscible solvent solution containing a multivalent reactant, such as a triacid chloride in hexane, which causes the monomer to polymerize and cross-link. Polymerization is confined to the interface of the two immiscible solutions, so a thin, highly selective layer is formed. The procedure is illustrated in **Figure 2**. The interfacial polymerization technique is used to produce most of today's reverse osmosis membranes.

Membrane Modules

The principal module designs – plate-and-frame, tubular, hollow-fibre and spiral-wound – are illustrated

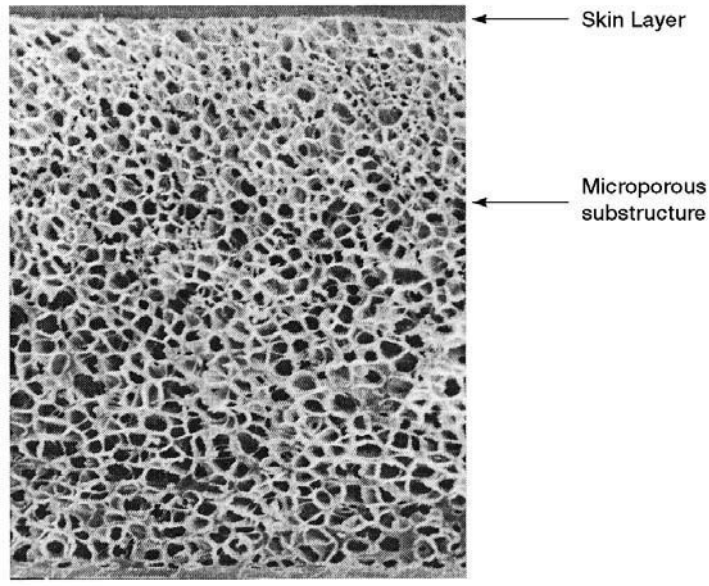

Figure 1 Scanning electron micrograph of the cross-section of a Loeb–Sourirajan reverse osmosis membrane. The development of this type of anisotropic membrane was a critical breakthrough in the development of membrane technology.

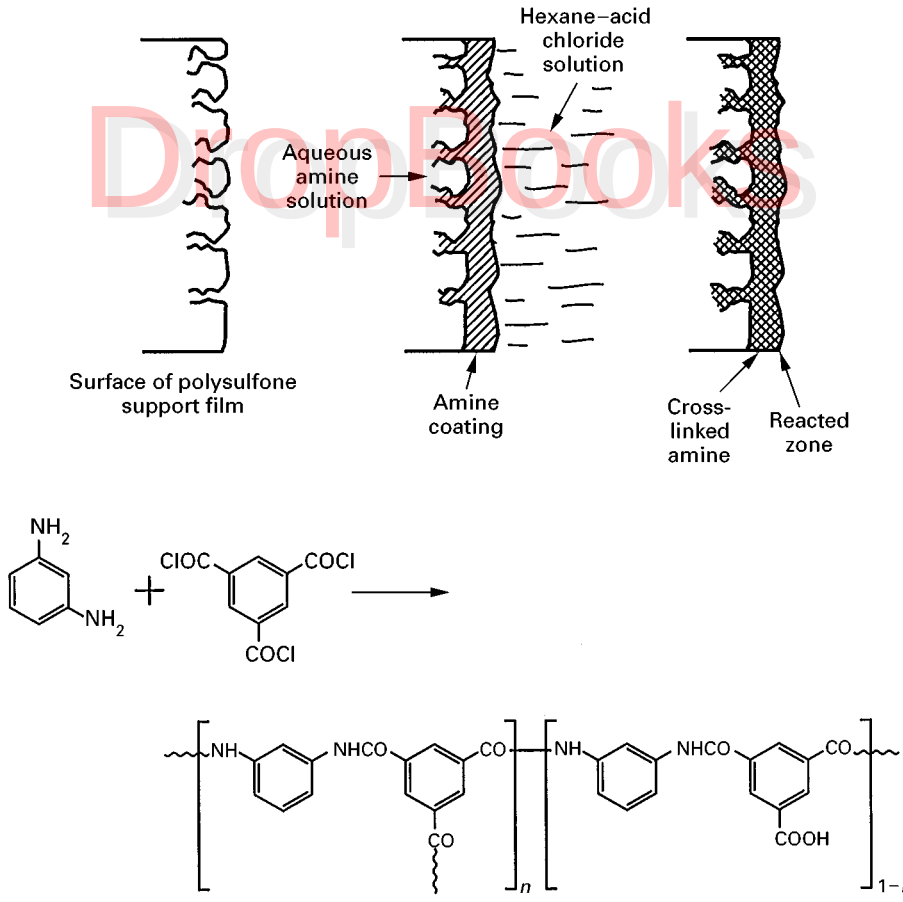

Figure 2 Preparation of ultrathin composite membranes by reaction of an amine dissolved in water and an acid chloride dissolved in hexane. The chemistry shown is widely used to prepare seawater desalination reverse osmosis membranes. (Reproduced with permission from Roselle LT *et al.* (1977). In: Sourirájan (ed.) *Reverse Osmosis and Synthetic Membranes.*)

in **Figures 3** and **4**. In the plate-and-frame design shown in Figure 3A a series of membrane discs separated by spacers and support plates are held between two end plates connected by a tension rod. The geometry of the plates is such that solution entering one end of the module passes sequentially over all the membrane area. Solution that permeates the membrane is collected in a permeate collection channel. Tubular modules shown in Figure 3B consist of a porous support tube, which is coated on the inside surface with the selective membrane. The porous support tube nests inside steel or strong plastic tubes that can support the applied pressure. Each tube is between 0.5 and 2 cm in diameter and up to five tubes can be housed in a single support tube. Tubular modules are now only used in ultrafiltration applications for which good flow distribution across the membrane surface with no stagnant areas is required to control membrane fouling. In this application up to 20 tubes are connected in series as shown in Figure 3B.

Plate-and-frame and tubular membranes were widely used in the early days of the modern membrane era, but by the 1980s had been largely displaced by hollow-fibre, capillary or spiral-wound membrane

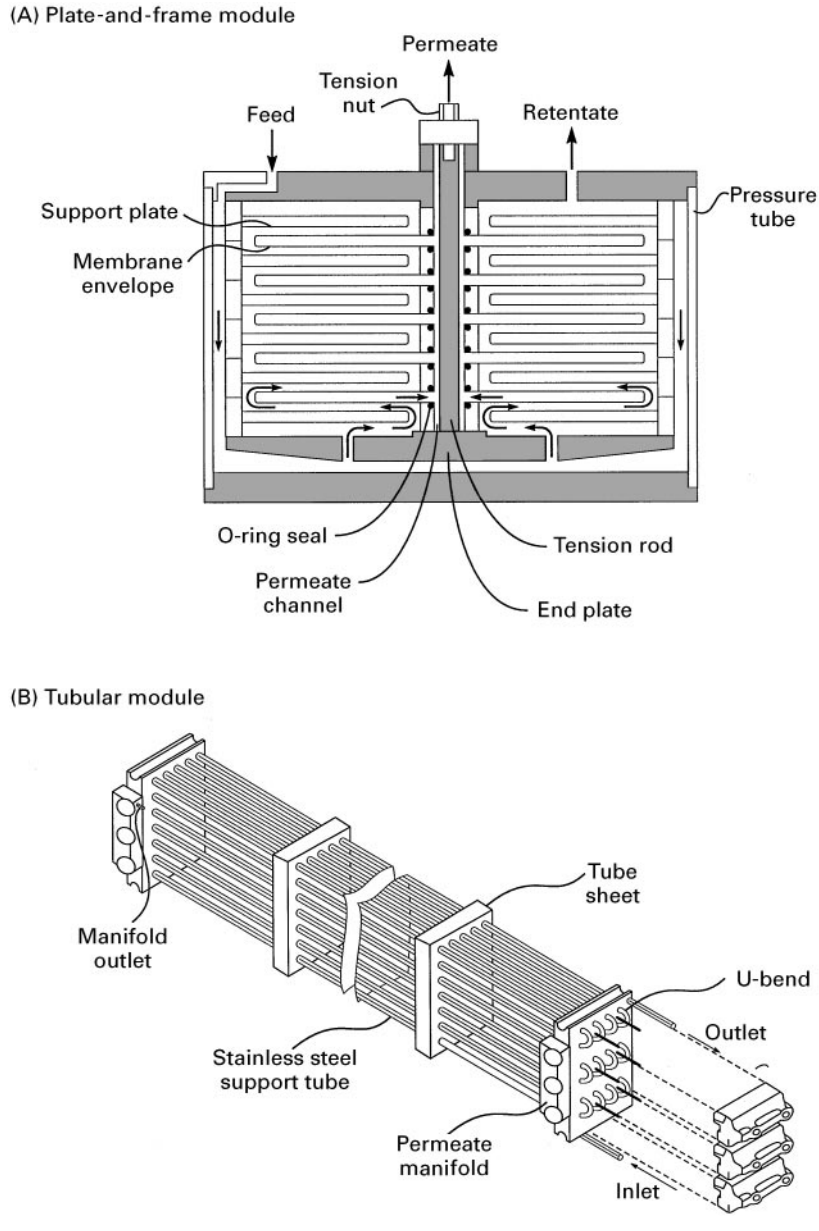

Figure 3 Schematic of a reverse osmosis plate-and-frame module (A) and a tubular ultrafiltration membrane module (B). These two module designs were used in the first large industrial membrane systems but are now limited to a few niche applications.

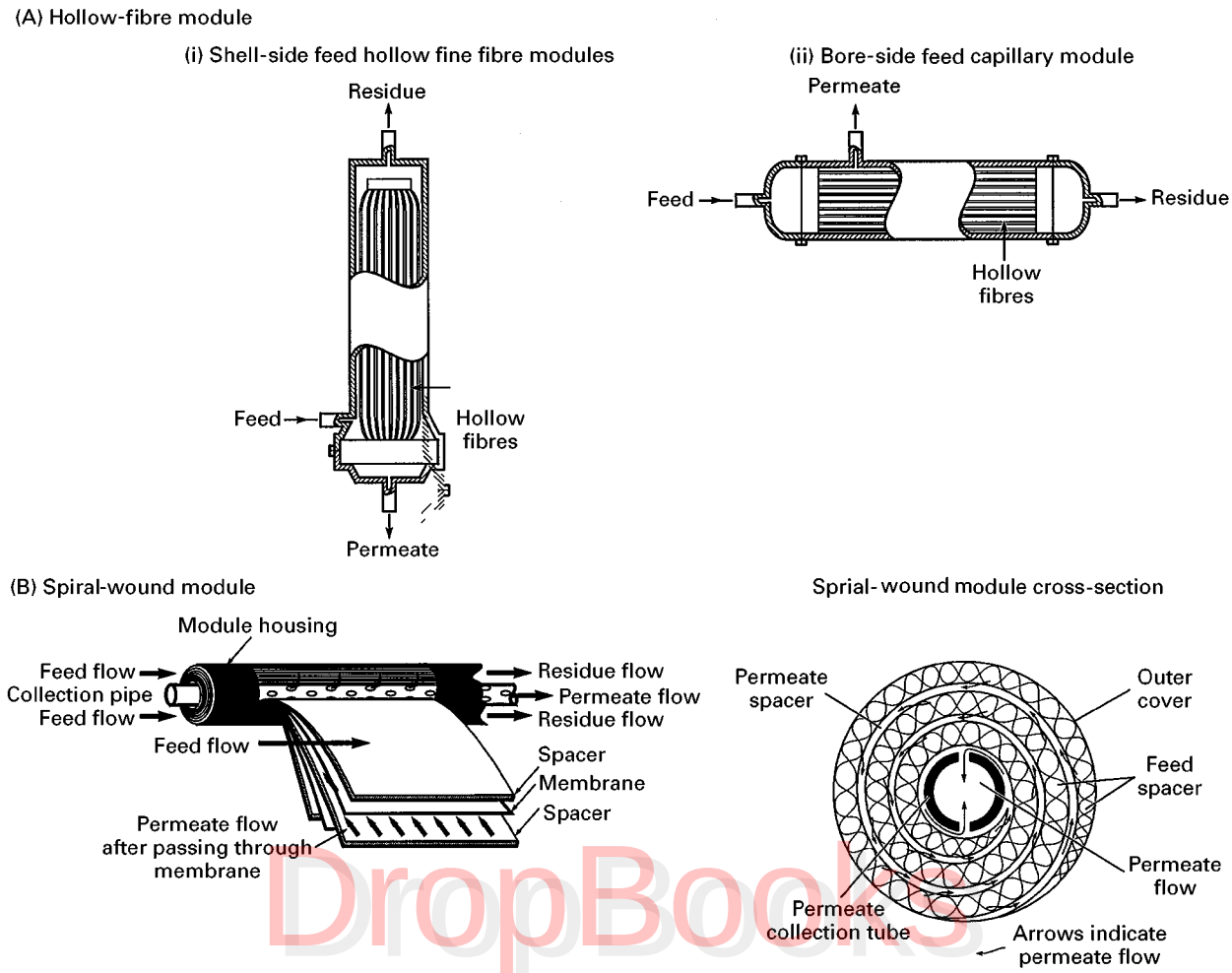

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Figure 4 Schematic illustrating hollow-fibre (A) and spiral-wound (B) membrane modules. Most large-scale membrane processes use one of the designs shown.

modules, which are much less expensive to produce per square metre of membrane area. Capillary and hollow-fine-fibre membranes are quite similar, differing principally in the diameter of the fibre used. Both types are produced by a spinning process much like conventional fibre spinning. As a result, the cost of producing the membrane per square metre is quite low. Most of the cost of producing hollow-fibres is incurred in the fibre potting operation when fibres are mounted inside the module shell. Currently, in capillary modules, the feed fluid circulates through the fibre lumen (bore side) as shown in Figure 4A. In hollow-fibre modules, the feed fluid circulates around the outer surface (shell side) of the fibres as shown in Figure 4B.

Spiral-wound modules were originally developed for reverse osmosis applications but are now used in ultrafiltration and gas separation processes as well. This work, carried out by Fluid Systems Inc. under sponsorship of the Office of Saline Water (later the Office of Water Research and Technology), resulted in a number of spiral-wound module designs. The design shown in Figure 4 is the most common, consisting of a membrane envelope wound around a perforated central collection tube. The module is placed inside a pressure vessel, and feed solution is circulated axially down the module across the membrane envelope. A portion of the feed permeates into the membrane envelope, spirals towards the centre of the module and exits through the collection tube.

The flat-sheet membranes used in spiral-wound modules usually have higher fluxes than capillary and hollow-fibre membranes made from the same material. This is because it is difficult to make hollow-fibre selective skins as thin as flat-sheet skins. For this reason, although spiral-wound modules are usually two to five times more expensive on a square metre basis than hollow-fibre membranes, they are competitive in many applications.

Membrane Selectivity

Improving membrane selectivity is still an area of active research. In some applications such as desalination of water, progress has been made, and membranes have the required selectivity to compete with other processes such as distillation. The first reverse osmosis membranes had salt rejections of approximately 96–97% and could only produce potable water from low concentration brackish water feeds. The best current membranes have salt rejections of up to 99.7% and can produce potable water from seawater. Further improvements in membrane selectivity are not required in this application.

In other applications, the low selectivity of membranes remains a problem. Ultrafiltration membranes, for example, cannot separate dissolved macromolecules, such as albumin (M_r 60 000) and γ-globulin (M_r 150 000). Therefore, ultrafiltration is limited to the separation of very large molecules from very small ones, such as macromolecules from dissolved micro-ions. Selectivity problems also exist in electrodialysis, gas separation and pervaporation.

Mechanism of Membrane Separation

The property of membranes used in separation processes is their ability to control the permeation of different species. Most membranes fall into one of the two broad categories illustrated in **Figure 5**. In microporous membranes, permeants are separated by pressure-driven flow through tiny pores. A separation is achieved between different permeants because one of the permeants is excluded (filtered) from some of the pores through which the smaller permeants move. In solution-diffusion membranes the membrane material is a dense polymer layer and contains no fixed pores. Permeants dissolve in the membrane material as in a liquid and then diffuse through the membrane down a concentration gradient. Separation of different permeants occurs because of differences in the solubility of the permeant in the membrane material and the rate at which the permeant diffuses through the membrane.

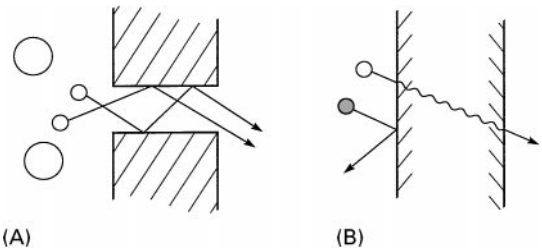

Figure 5 Schematic illustrating the two principal types of membrane separation mechanisms. (A) Microporous membranes separate by molecular filtration. (B) Dense solution-diffusion membranes separate because of differences in the solubility and mobility of permeant in the membrane material.

The difference between the pore-flow and the solution-diffusion mechanisms lies in the relative size and lifetime of pores in the membrane. In dense polymeric solution-diffusion membranes, no permanent pores exist. However, tiny free volume elements, a few tenths of a nanometre in diameter, exist between the polymer chains from which the membrane is made. These free-volume elements are present as statistical fluctuations that appear and disappear on a timescale only slightly slower than the motion of molecules traversing the membrane. Permeating molecules diffuse from free-volume element to free-volume element at a rate determined by the thermal motion of the polymer chains from which the membrane is made. In contrast, in a pore-flow membrane the pores are fixed and do not fluctuate in position or size on the timescale of molecular motion. The larger the individual free-volume elements are, the more likely they are to be present long enough to produce pore-flow characteristics in the membrane. As a rule of thumb the transition between permanent (pore-flow) and transient (solution-diffusion) pores appears to be in the range 0.5–1.0 nm diameter. This means that the processes of gas separation, reverse osmosis and pervaporation, all of which involve separation of permeants with molecular weights of less than 200, use solution-diffusion membranes. On the other hand, microfiltration and ultrafiltration, which involve separation of macromolecular or colloidal material, use finely microporous pore-flow membranes.

Commercial Membrane Separation Processes

The current status of membrane separation technology is summarized in **Table 1**. There are seven commercial membrane separation processes. Of these, the first five – microfiltration, ultrafiltration, reverse osmosis, electrodialysis and dialysis – are all well-established technologies with a market served by several experienced companies. Although incremental improvements in membranes and membrane systems for these technologies are expected, no major breakthroughs appear imminent. The remaining two technologies – gas separation and pervaporation – are developing technologies for which the market size, application area, and process design are still changing. Finally, several processes not shown in Table 1, including coupled and facilitated transport, membrane contactors and membrane reactors, are still in

Table 1 Summary of the established membrane separation technologies

Process	*Type of membrane*	*Material passed*	*Material retained*	*Driving force*	*Status – typical application*
Microfiltration	Finely microporous 0.1–10 μm	Water, dissolved solutes	Suspended solids, bacteria	Pressure difference 5–50 psi	Developed (~US$700 million per year). Removal of suspended solids, bacteria in pharmaceutical, electronics industries
Ultrafiltration	Finely microporous 1–100 nm	Water, dissolved salts	Macromolecules, colloids	Pressure difference 20–100 psi	Developed (~US$150 million per year). Removal of colloidal material from wastewater, food process streams
Reverse osmosis	Dense solution-diffusion	Water	Dissolved salts	Pressure difference 100–1000 psi	Developed (~US$200 million per year). Drinking water from sea, brackish or groundwater; production of ultrapure water for electronics and pharmaceutical industries
Electrodialysis	Electrically charged films	Water	Ions	Voltage difference 1–2 V	Developed (~US$200 million per year). Drinking water from brackish water; some industrial applications too
Dialysis	Finely microporous 10–100 nm	Dissolved salts, dissolved gases	Blood	Concentration differences	Developed (~US$1.3 billion per year for artificial kidney; US$500 million per year for artificial lung)
Gas separation	Dense, solution-diffusion	Permeable gases and vapours	Impermeable gases and vapors	Pressure difference 100–1000 psi	Developing (~US$150 million per year). Nitrogen from air, hydrogen from petrochemical/refinery vents, carbon dioxide from natural gas, propylene and VOCs from petrochemical vents
Pervaporation	Dense, solution-diffusion	Permeable micro-solutes and solvents	Impermeable micro-solutes and solvents	Vapour pressure 1–10 psi	Developing (~US$10 million per year). Dehydration of solvents (especially ethanol)

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the laboratory or early commercial stage. In the following sections each of these membrane technology areas is described briefly. More detailed descriptions of the more important processes are given elsewhere in the encyclopedia.

Microfiltration

The process Microfiltration, ultrafiltration and reverse osmosis are related membrane processes differing in the size of the material retained by the membrane. As shown in **Figure 6**, reverse osmosis membranes can generally separate dissolved microsolutes with a molecular weight below 500 by a solution-diffusion mechanism. When the molecular weight of the solute exceeds 500, the separation mechanism of the membrane is molecular filtration, in which separation characteristics are determined by the size of the particles in the mixture and the diameter of the pores in the membrane. By convention, membranes having pore sizes up to approximately 0.1 μm in diameter are considered to be ultrafiltration membranes. Microfiltration membranes are those with pore diameters in the range of 0.1 to 10 μm. Above 10 μm the separation medium is considered to be a conventional filter.

Ultrafiltration/microfiltration membranes fall into two broad categories: screen membrane and depth membrane filters, as shown in **Figure 7**. Screen filters are anisotropic with small surface pores on a more open substructure. The surface pores in screen membrane filters are uniform and show a sharp cutoff between material that is completely retained by the membrane and material that penetrates the membrane. Retained material accumulates on the membrane surface. Depth membrane filters have a much wider distribution of pore sizes and usually have a more diffuse cutoff than screen membrane filters. Very large particulates are retained on the surface of the membrane, but smaller particulates entering the membrane are trapped at constrictions or adsorbed onto the membrane surface. Screen filters are usually used in ultrafiltration applications (see next section). The membrane pores are normally very small, on the order of 5–50 nm in diameter. Particulates and colloidal matter retained at the membrane surface are removed by a tangential flow of the feed solution. In this type of process, 80–90 vol% of the

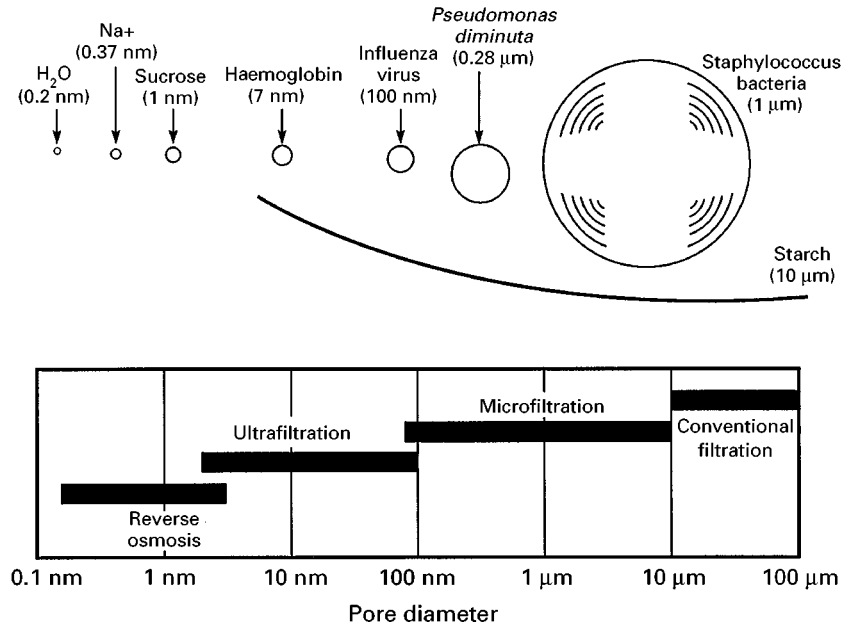

Figure 6 Pore sizes of reverse osmosis, ultrafiltration, microfiltration and conventional filtration membranes.

feed solution permeates the membrane as a clean filtrate. The remaining solution containing the rejected material is collected as a concentrated residue.

Depth filters are usually used in microfiltration applications. The surface membrane pores can be quite large, on the order of 1–10 μm in diameter, but many smaller restrictions occur in the interior of the membrane. This means that bacteria or virus particles as small as 0.2 μm in diameter are completely prevented from penetrating the membrane. Microfiltration membranes are usually used as an in-line filter. All of the feed solution is forced through the membrane by an applied pressure. Retained particles are collected on or in the membrane.

The lifetime of microfiltration membranes is often improved by using a more open prefilter membrane directly before the final membrane. Prefilters are not absolute filters, but trap most of the very large particulates and many of the smaller ones before the feed solution reaches the finer membrane filter. This reduces the particle load that the finer membrane must handle, and thus increases its useful life.

Applications The primary market for microfiltration membranes is disposable cartridges for sterile filtration of water for the pharmaceutical industry and final point-of-use polishing of ultrapure water for the electronics industry. The cost of microfiltration compared with the value of the products is small. Cold sterilization of beer, wine and other beverages is another emerging market area. In these processes the microfiltration cartridge removes all yeast and

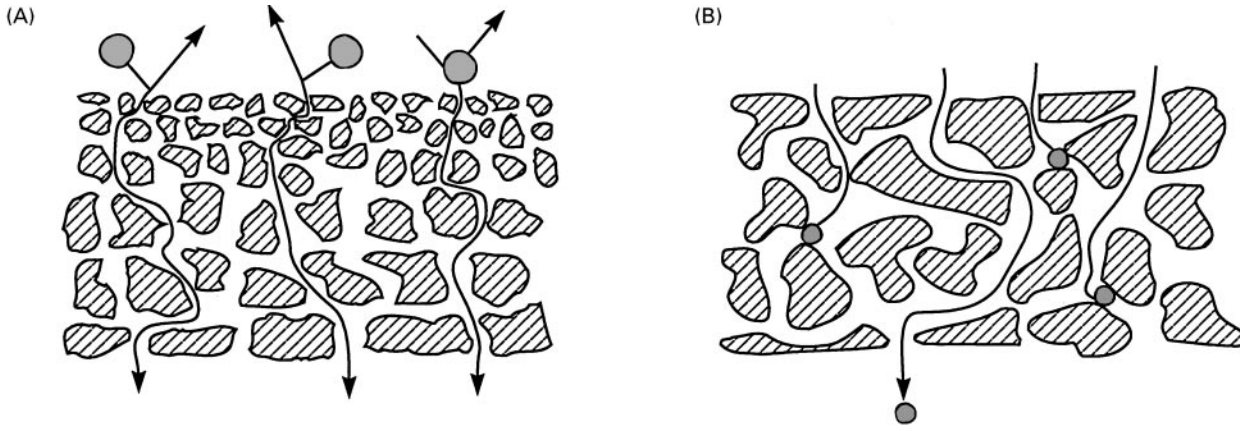

Figure 7 Separation of particulates can take place at the membrane surface according to a screen filtration mechanism (A) or in the interior of the membrane by a capture mechanism as in depth filtration (B).

bacteria from the filtrate. This process was introduced on a commercial scale in the 1960s. Although not generally accepted at that time, the process has become common in recent years.

Ultrafiltration

The process Ultrafiltration is intermediate between microfiltration and reverse osmosis. The most retentive ultrafiltration membrane has a substantial rejection to microsolutes, such as raffinose (M_r 504), while the most open ultrafiltration membrane will be just able to retain a molecule of relative molecular mass one million. In practice, the distinction between ultrafiltration, reverse osmosis and microfiltration is vague, and it is possible to prepare membranes covering the entire range of reverse osmosis, ultrafiltration and microfiltration by making small changes in membrane preparation procedures.

Essentially all ultrafiltration membranes are screen filtration membranes and separate the retained material because of the small pores in their top surface layer (see Figure 7A). Membranes are characterized by their molecular weight cutoff, which is usually defined as the molecular weight at which the membrane retains more than 95% of the test solute. The definition is ambiguous, because flexible-backboned, linear molecules can penetrate membranes more easily than rigid, globular molecules, such as dissolved proteins. In addition, despite the claims of the manufacturers, no ultrafiltration membrane has a perfectly sharp molecular weight cutoff. All membranes contain a range of pore sizes and the passage of molecules through the pores is completely unhindered only for very small molecules. Typical molecular weight cutoff curves for a series of commercial membranes are shown in **Figure 8**.

Ultrafiltration systems generally operate at pressures of 20–100 psi (140–690 kPa). Osmotic pressure effects are not significant in ultrafiltration, and high operating pressures are not required to produce high fluxes. Moreover, because of their porous structure, ultrafiltration membranes compact under pressures above 100 psi (690 kPa).

The most important problem associated with ultrafiltration membranes is surface fouling. The problem is illustrated in **Figure 9**. Material unable to pass through the membrane accumulates at the surface, forming a solid gel-like film that acts as a barrier to the flow of permeate through the membrane. The thickness of the fouling film is controlled by the sweeping action of the feed solution past the membrane surface. This circulating flow of solution hydrodynamically scrubs the membrane surface, continuously removing the surface film. Thus a balance is

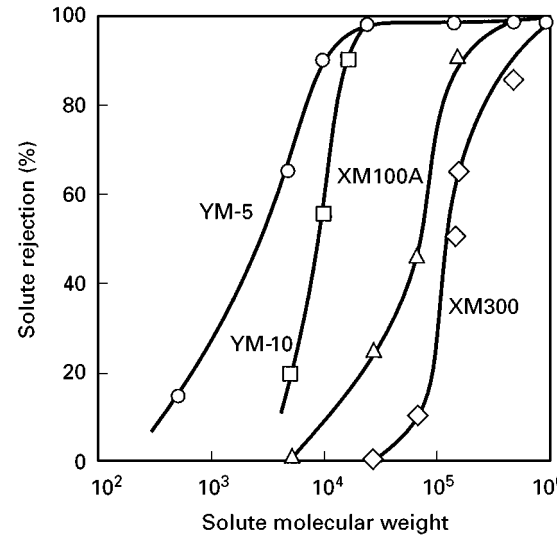

Figure 8 Molecular weight cuttoff curves of various ultrafiltration membranes. (Amicon Corporation trade literature.)

achieved between circulation of solution past the membrane surface, which removes the gelled material, and the flux of permeate through the membrane, which brings fresh material to the membrane surface. Therefore, in ultrafiltration, only a portion of the feed

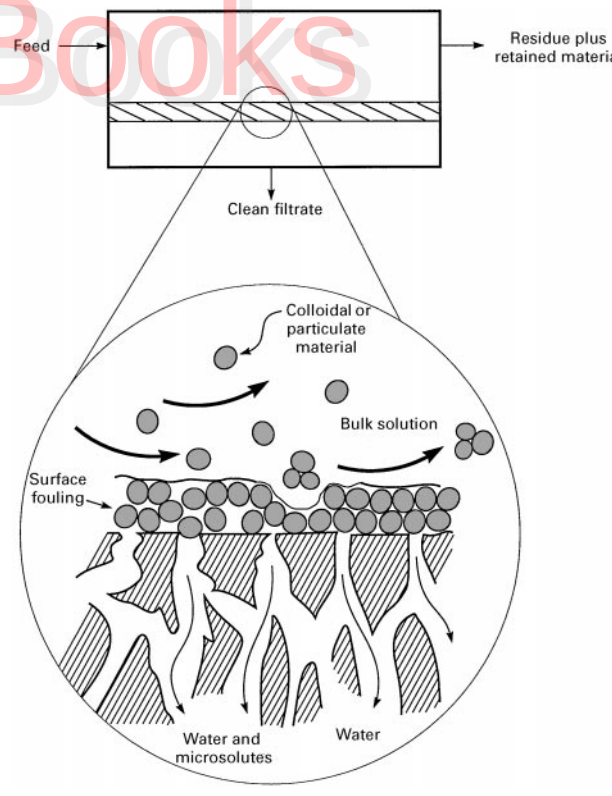

Figure 9 Schematic of ultrafiltration illustrating the dynamic process of deposition and removal of particulate and colloidal material from the surface of the membrane.

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solution permeates the membrane; the remaining solution, containing the retained material, is removed as a concentrated residue stream.

If the feed solution circulation rate across the membrane surface is increased, the thickness of the fouling layer on the membrane surface decreases, and higher permeate fluxes through the membrane are obtained. However, at some point the increased energy cost involved in recirculating the feed solution offsets the savings produced by the higher membrane fluxes. With highly fouling solutions, energy consumption of 30–100 kWh per 1000 gallons (30–100 MJ m^{-3}) of permeate produced is typical. The resulting electric energy expense represents a large fraction of the operating cost of an ultrafiltration plant. Increasing the operating pressure of the membrane system to force more permeate through the membrane is not a viable method of increasing the membrane flux because this only produces a thicker gel layer on the membrane surface so that the flux remains constant or even declines.

Even when most of the layer of deposited material on the membrane surface is continuously removed, a portion remains and gradually densifies. This results in decreased permeate flux through the membrane with time. Periodically, ultrafiltration membrane modules are cleaned by washing with a membrane-cleaning solution. This restores the flux to almost its original value, after which the flux begins to decline again. The process is illustrated in **Figure 10**. Unfortunately, cleaning of badly fouled membranes does not completely restore the flux to the starting value so that a proportion of the membrane flux is permanently lost. This permanent loss results from deposits of fouling material inside the membrane, which cannot be removed even by vigorous cleaning. The fouling material gradually accumulates until even the flux of a freshly cleaned membrane is less than 50% of the original value. At this time, the membrane is due for replacement. A typical ultrafiltration membrane lifetime is 1–3 years.

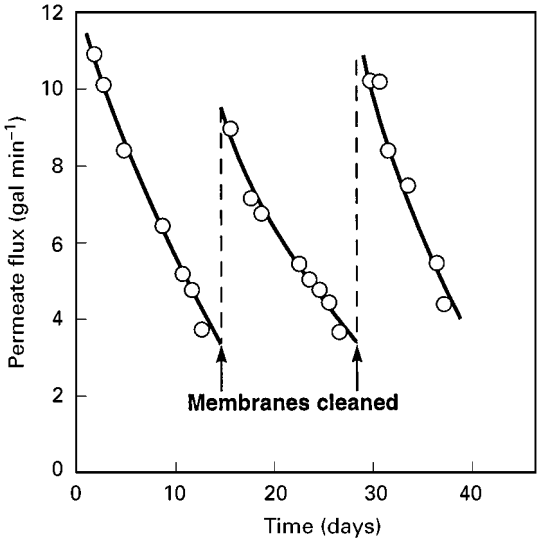

Figure 10 Ultrafiltration flux as a function of time for an electrocoat paint latex solution. Fouling causes flux decline in a matter of days. Periodic cleaning is required to maintain high fluxes.

Because of membrane fouling, the flux of ultrafiltration membranes depends highly on the composition of the feed solution and the process operating conditions. In the removal of trace particulates for the preparation of ultrapure water, the feed solution is already clean, and fluxes higher than 50–100 gal per ft^2 per day (85–170 L per m^2 per day) are achieved. With more concentrated and contaminated solutions, such as food processing streams, industrial wastewaters, or electrocoat paint wastes, typical fluxes are 10–30 gal per ft^2 per day (17–50 L per m^2 per day).

Applications Ultrafiltration membranes were originally developed for the laboratory market and found an application in the concentration and desalting of protein solutions. Later, Abcor and Romicon developed the industrial ultrafiltration market. The first major application was the ultrafiltration of electrocoat paint. The process is illustrated in **Figure 11**. In electrocoat paint operations metal parts are immersed in a tank containing 15–20% of the paint emulsion. After coating, the piece is removed from the tank and rinsed to remove excess paint. The ultrafiltration system removes ionic impurities from the paint tank carried over from earlier operations and provides clean rinse water for the countercurrent rinsing operation. The concentrated paint emulsion is recirculated back to the tank. Tubular and capillary fibre membrane modules are generally used in these plants because the feed solution easily fouls the membrane. Other large applications of ultrafiltration are the concentration of milk whey in the food industry to recover milk proteins and to remove lactose and salts in the membrane filtrate, and the concentration of oil emulsions in the metal finishing industry. Although some ultrafiltration plants treat industrial waste streams, this is not a common application because the process is expensive. The preparation of ultrapure water by ultrafiltration for the electronics industry is a newer, but growing, application. Biotechnology applications are, as yet, small.

The problem of membrane fouling in ultrafiltration systems requires expensive, energy-consuming pumps to recirculate the feed solution. Costs of ultrafiltration systems are on the order of US$5–10 per 1000 gal of permeate, precluding its use in large, low-value applications such as wastewater treatment.

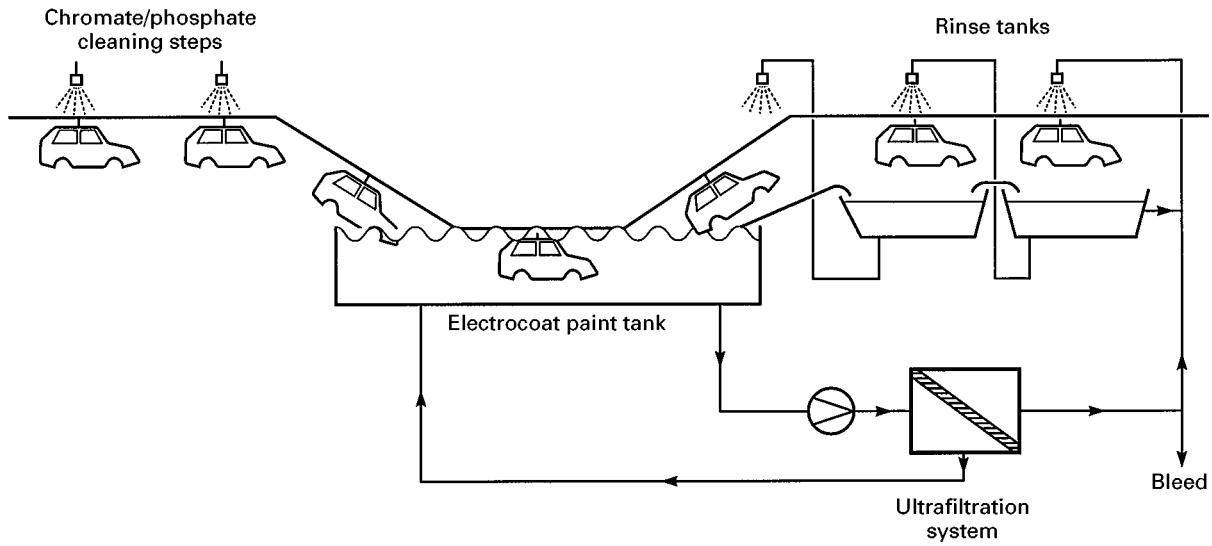

Figure 11 Flow schematic of an electrocoat paint ultrafiltration system. The ultrafiltration system removes ionic impurities from the paint tank carried over from the chromate/phosphate cleaning steps and provides clean rinse water for the countercurrent rinsing operation.

Therefore, ultrafiltration is limited to the type of high-value streams listed above. Development of more fouling-resistant membranes and better module designs could allow wider use of the process.

Reverse Osmosis

The process The processes of osmosis and reverse osmosis are illustrated in Figure 12. In normal osmosis, a membrane is used to separate water from a salt solution. If the membrane is semipermeable, that is, it allows the passage of water but does not pass salt, the small difference in water concentration (salt solution) will cause water to flow into the salt side of the membrane. This flow will continue until the hydrostatic pressure head on the salt solution exactly balances the flow of water across the membrane. This balance is known as osmotic equilibrium. In reverse osmosis, a pressure is applied to the salt solution that is even higher than the osmotic pressure of the solution. This applied pressure reverses the osmotic water flow, and water flows from the salt solution to the pure water side of the membrane. Therefore, reverse osmosis is a method of desalting saltwater solutions. Equilibrium osmotic pressures are directly proportional to salt concentration and are surprisingly large. For example, the osmotic pressure for sodium chloride is approximately 100 psi (690 kPa) for a 1% salt solution.

Two parameters affect the performance of reverse osmosis membranes. The first is the flux or flow per unit area per time, J, of water through the membrane, usually described by the equation:

$$J = A(\Delta P - \Delta\pi) \qquad [1]$$

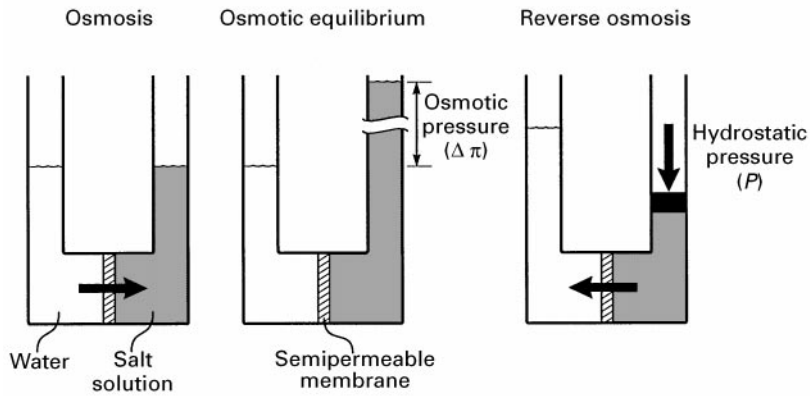

Figure 12 Osmotic effects across a semipermeable membrane. (Reprinted with permission from Roper and Lightfoot (1995) *Journal of Chromatography* 702: 3–26, with permission from Elsevier Science.)

where A is the hydrodynamic water permeability parameter, ΔP is the pressure difference across the membrane, and $\Delta\pi$ is the osmotic pressure difference across the membrane. Thus, once the osmotic pressure of the salt solution has been overcome, the water flux increases linearly with applied pressure. The salt flux through reverse osmosis membranes, J_s, is proportional to the salt concentration differences (ΔC) across the membrane, but is independent of the applied pressure. Thus:

$$J_s = B(\Delta C) \qquad [2]$$

where B is the salt permeability factor. This means that the performance of reverse osmosis membranes, as measured by the salt rejection, improves as the applied pressure increases. Therefore, reverse osmosis membranes are usually operated at high pressures to obtain the maximum throughput commensurate with reasonable capital and energy costs. With current membranes, operating pressures are usually between 200 (1380) and 800 psi (5520 kPa).

The second parameter that affects membrane performance is the salt passage through the membrane. Ideally, the membrane should be completely selective for salt. This is never the case, and a small fraction of the salt passes through the membrane. The fraction that appears in the product is usually measured in terms of the rejection coefficient of the membrane, defined as:

$$R = [(\text{salt concentration in feed} - \text{salt concentration in product})/\text{salt concentration in feed}] \times 100\% \qquad [3]$$

Thus, a completely selective membrane has a rejection of 100%, whereas a completely nonselective membrane has a rejection of 0%. A typical plot of flux and rejection versus operating pressure is shown in **Figure 13**.

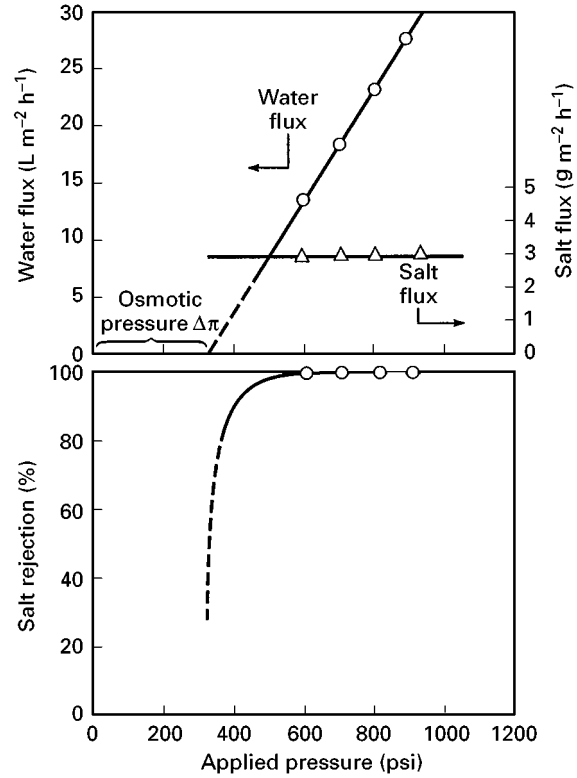

Figure 13 Flux and rejection data for a model seawater solution (3.5% sodium chloride) in a good quality reverse osmosis membrane (FilmTec Corp. FT 30 membrane) as a function of pressure. The salt flux, in accordance with eqn [2], is essentially constant and independent of pressure. The water flux, in accordance with eqn [1], increases with pressure, and, at zero flux, meets the pressure axis at the osmotic pressure of seawater ~ 350 psi. (Reprinted from Wijmans JG and Baker RW (1995) The solution-diffusion model: a review. *Journal of Membrane Science* 107: 1–21, with permission of Elsevier Science.)

The first successful reverse osmosis membranes were made by Loeb and Sourirajan and had rejections in the range 97–98%. These membranes produced potable water (less than 500 ppm salt) from feed water containing up to 1% salt. This salt concentration is typical of many brackish groundwaters, so these membranes found an immediate application in the desalination of such waters. However, production of potable water from seawater requires a membrane with a salt rejection of greater than 99%. Loeb–Sourirajan cellulose acetate membranes can be modified to obtain this rejection, but only by reducing membrane flux to uneconomically low values. In the mid-1970s, Du Pont produced improved polyamide hollow-fibre membranes (the B10 Permeator) which had greater than 99% rejection. At about the same time, interfacial polymerization composite membranes were produced by Cadotte at North Star Research. These composite membranes had salt rejections greater than 99%, and subsequent improvements have raised these rejections to 99.5–99.8%. Interfacial composite membranes have now become the industry standard; three-quarters of current reverse osmosis membranes are of this type.

Reverse osmosis membranes are produced in several module configurations. Most of the modules used are of the spiral-wound type, which has 80% of the market. Hollow-fibre membrane modules are generally limited to seawater reverse osmosis plants. A few plate-and-frame and tubular modules are used in food processing and the treatment of industrial wastewater, which usually contain high levels of suspended solids and require this type of nonfouling module.

Applications Approximately half of the reverse osmosis systems currently installed are desalinating

brackish water or seawater. Another 40% are used to produce ultrapure water for electronics, pharmaceuticals and power generation. The remainder are used in small niche applications such as pollution control and food processing.

Brackish water desalination The salinity of brackish groundwater is usually between 1500 and 5000 mg L^{-1}. The World Health Organization recommends that drinking water should contain less than 500 mg L^{-1} salt, so up to 90% of the salt must be removed from these waters. This is easily achieved by reverse osmosis. A typical process flow scheme is shown in **Figure 14**. Frequently brackish water is contaminated with suspended solids, so flocculation, sand filtration, and a final cartridge filter are used to remove these components first. Adjustment of pH and addition of antiscalants may also be necessary to prevent calcium, magnesium or silica precipitating on the membrane as water is removed and the feed becomes more concentrated. The water may also be sterilized by addition of chlorine to prevent bacterial growth on the membrane. Even when these elaborate and costly feed water pretreatment steps are used, some fouling of the membrane still occurs. Therefore, periodically the plant is taken off-line and the membranes are cleaned by circulating a hot cleaning solution. Typical operating pressures for these systems are in the 200–300 psig range. Plant capital costs are in the range US$1.00–2.00 per gal per day (plant) capacity, and operating costs are about US$1–2 per 1000 gal of treated water produced. Well-maintained plants have useful membrane lifetimes of 3–5 years.

Seawater desalination Seawater contains about 3.5% dissolved salt, which means membranes with salt rejections above 99.3% are required to produce potable water. Today's membranes can easily meet these targets, and many seawater desalination plants are now operating. Because of the high osmotic pressure of seawater (~ 350 psi (2415 kPa)) these plants operate at pressures of 800–1000 psi (5520–6900 kPa). Typical seawater reverse osmosis plants have a capital cost of US$4–5 gal per day capacity and produce desalted water for a cost of about US$5 per 1000 gal of product. These costs mean the process is most competitive for systems below 10 million gal per day capacity. Above this range economies of scale tend to favour multi-effect evaporation plants often built to use the waste heat from electric power stations.

Ultrapure water With the development of the electronics industry, a large market has emerged for reverse osmosis plants to produce ultrapure water containing < 1 ppb total ions from water normally containing 50–100 ppm total ions. Typical operating pressures for the reverse osmosis systems used in these plants are low, on the order of 100–150 psi (690–1035 kPa). The reverse osmosis plant removes 98–99% of the salts and dissolved particles in the feed

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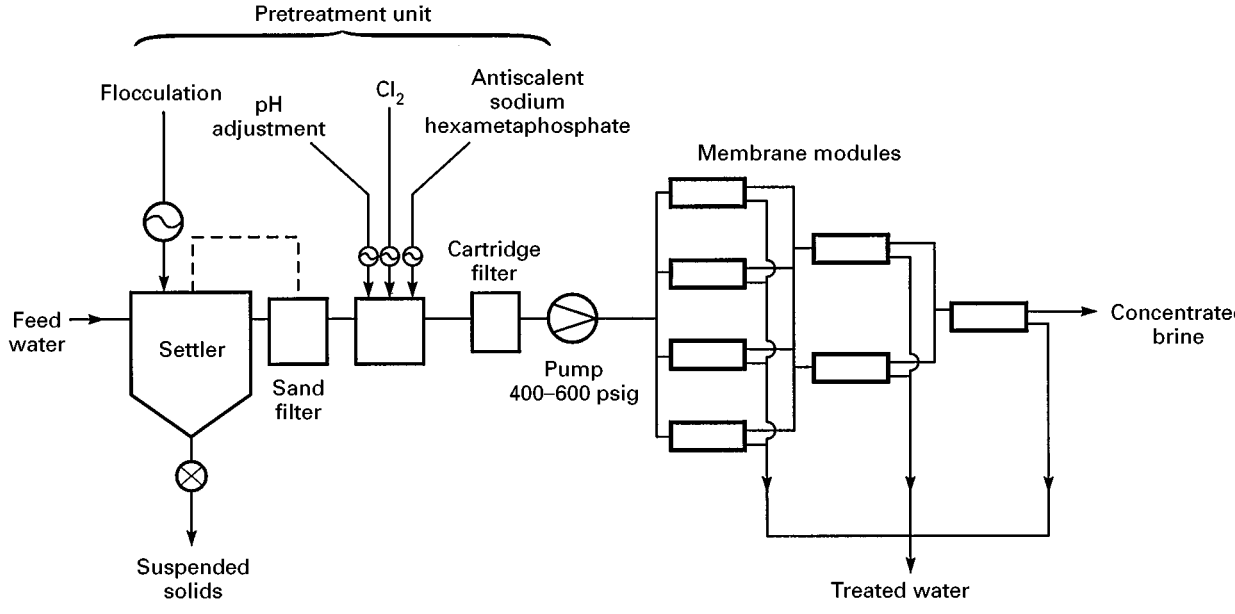

Figure 14 Flow schematic of a brackish water reverse osmosis plant. The plant contains seven pressure vessels each containing six membrane modules. The pressure vessels are arranged in a Christmas tree array to maintain a high feed velocity through the modules as treated water is removed in the permeate.

water. Carbon adsorption and ion exchange units are used to remove the remaining contaminants.

Electrodialysis

The process Electrodialysis is a process in which electrically charged membranes are used to separate ions from aqueous solutions under the driving force of an electrical potential difference. The process, illustrated in **Figure 15**, utilizes an electrodialysis stack built on the filter press principle. The stack consists of 200–400 alternate cationic and anionic membranes between two electrodes; the aqueous feed solution flows through the cells between each pair of membranes. When an electrical potential difference is applied between the two electrodes, positively charged cations in the feed solution move toward the cathode. These ions easily pass through the negatively charged cation exchange membranes, but are retained by the positively charged anion exchange membranes. Similarly, negatively charged anions migrate towards the anode, pass through the anion exchange membrane and are retained by the cation exchange membrane. Because of the arrangement of ion-selective membranes, the migrating ions become concentrated in each alternate cell in the stack. Thus, ions removed from the aqueous feed solution are concentrated into two separate streams.

Applications

Brackish water Brackish water desalination is the largest application of electrodialysis. The competitive technologies are ion exchange for very dilute solutions (below 500 ppm) and reverse osmosis for solutions above 2000 ppm salt. In the 500–2000 ppm range, electrodialysis is almost always the lowest cost process. One advantage of electrodialysis when applied to brackish water desalination is that a large fraction, typically 80–95% of the brackish feed, is recovered as potable water. However, these high recoveries mean that the concentrated brine stream produced is 5–20 times more concentrated than the feed. Precipitation of insoluble salts in the brine can limit the water recovery.

Since the first electrodialysis plants were produced in the early 1950s, several thousand brackish water

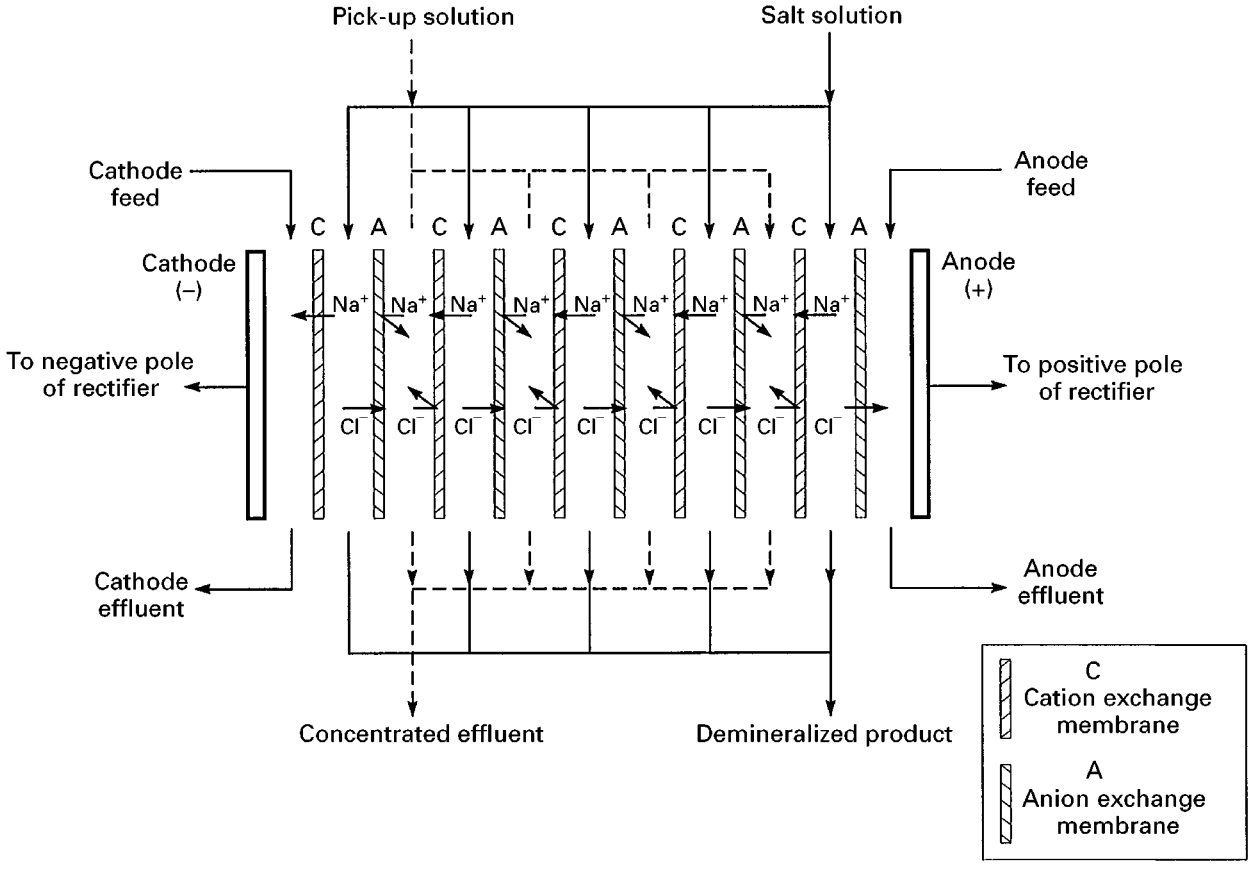

Figure 15 Schematic diagram of a plate-and-frame electrodialysis stack. Alternating cation- and anion-permeable membranes are arranged in a stack of up to 100 cell pairs.

electrodialysis plants have been installed around the world. Modern electrodialysis units are generally fully automated and require only periodic operator attention. This has encouraged installation of many small trailer-mounted plants. However, a number of very large plants with production rates of 10 million gal per day or more have also been produced.

The power consumption of an electrodialysis plant is directly proportional to the salt concentration in the feed water, and varies from 4 kWh per 1000 gal (4 MJ m^{-3}) for 1000 ppm feed water to 10–15 kWh per 1000 gal (10–15 MJ m^{-3}) for 5000 ppm feed water. About one-quarter to one-third of this power is used to drive the feed water recirculation pumps.

Seawater A second major application of electrodialysis is the production of table salt by concentration of seawater. This process is only practised in Japan, which has no other domestic salt supply. The process is heavily subsidized by the government. Total production is approximately 1.2 million tons per year of salt, with more than 500 000 m^2 of membrane used in the plants.

A flow scheme for one such seawater salt-production plant is shown in **Figure 16**. A cogeneration power plant produces the power required for the electrodialysis operation, which concentrates the salt in seawater to about 18–20 wt%. Waste steam from the power plant is then used to concentrate the salt further by evaporation.

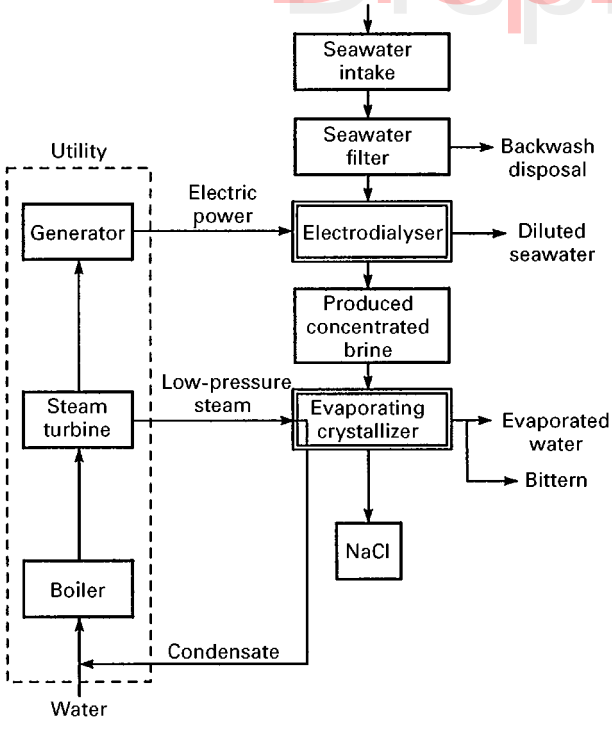

Figure 16 Flow scheme of a typical electrodialysis process used in a seawater salt concentration plant.

Gas Separation

The process The study of gas permeation through membranes has a long history dating back to the work of Thomas Graham in the mid-nineteenth century. However, the first systematic studies with polymers of the type used today did not begin until 100 years later.

The mechanism of gas permeation developed in the 1950s and 1960s was the solution-diffusion model. In this model, the rate of diffusion through the polymer membrane is governed by Fick's law of diffusion. For simple gases, it can be shown that Fick's law leads to the expression

$$J = \frac{Dk\Delta p}{l} \qquad [4]$$

where J is the membrane flux (cm^3(STP)/cm^2 s), k is the Henry's law sorption coefficient linking the concentration of gas in the membrane material to the pressure of the adjacent gas (cm^3(STP)/cm Hg), Δp is the partial difference across the membrane, l is the membrane thickness (cm), and D is the permeant diffusion coefficient ($cm^2\ s^{-1}$), a measure of the permeant's mobility in the membrane. This expression can be further simplified to

$$J = \frac{P\Delta p}{l} \qquad [5]$$

where P is a permeability, equal to the product Dk, and is a measure of the rate at which a particular gas moves through the membrane of a standard thickness (1 cm) under a standard driving pressure (1 cm Hg). The permeability unit, 1×10^{-10} cm^3 (STP) cm/cm^2 s cm Hg, is called a Barrer, after R.M. Barrer, a pioneer in membrane permeation studies.

A measure of the ability of a membrane to separate two gases (1) and (2) is the ratio of their permeabilities, called the membrane selectivity, α:

$$\alpha_{1,2} = \frac{P_1}{P_2} = \frac{D_1}{D_2} \times \frac{k_1}{k_2} \qquad [6]$$

The factors that determine membrane permeability can best be understood by considering the component terms D and k. For simple gases, the diffusion coefficient tends to decrease with increasing permeant diameter, because large molecules interact with more segments of the polymer chains and are thus less mobile. On the other hand, the sorption

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coefficient of gases increases with the condensability of the gas. Normally, the sorption coefficient also correlates with molecular diameter, larger molecules being more condensable than smaller molecules, and the Henry's law sorption coefficient increases with increasing permeant diameter. Thus, the effect of increasing permeant size on permeability is a balance between the opposing effects of diffusion coefficient, which decreases with increasing size, and solubility, which increases with increasing size. This balance determines the selectivity of a membrane for any pair of gases and is a function of the membrane material.

In glassy, rigid polymers such as polysulfone or polyimides, permeant diffusion coefficients are most important. Therefore, these polymers preferentially permeate the small, noncondensable gases, hydrogen, nitrogen and methane, over the larger, condensable gases, propane and butane. On the other hand, in rubbery polymer such as silicone rubber (polydimethylsiloxane), permeant solubility coefficients are most important. Therefore, these polymers preferentially permeate the larger, more condensable gases, propane and butane, over the smaller, noncondensable gases, hydrogen, nitrogen and methane.

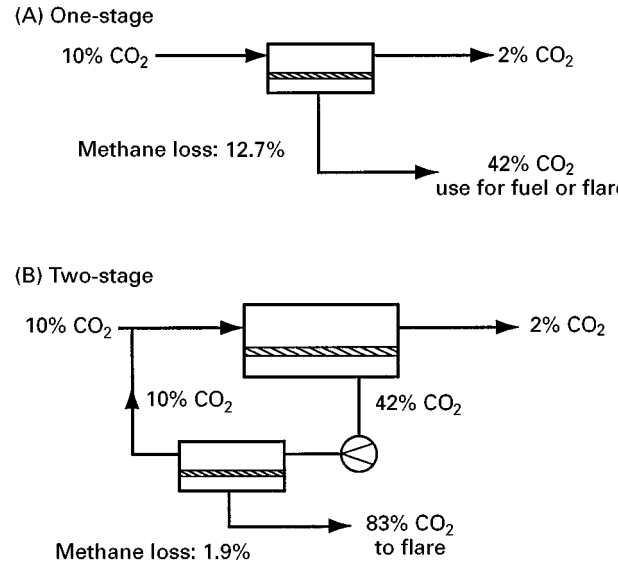

Figure 17 Flow scheme of (A) a one-stage and (B) a two-stage membrane gas separation system for the separation of carbon dioxide from natural gas.

Applications The principal developed gas separation processes are listed in **Table 2**. The first large-scale commercial application of gas separation was the separation of hydrogen from nitrogen in ammonia purge gas streams. The process, launched in 1980 by Permea, then a Division of Monsanto, was followed by a number of similar applications, such as hydrogen/methane separation in refinery off-gases and hydrogen/carbon monoxide adjustment in oxo-chemical synthetic plants.

Following Permea's success, several US companies produced membrane systems to treat natural gas streams, particularly to remove carbon dioxide. The goal is to produce a stream containing less than 2% carbon dioxide to meet the national pipeline specifications and a permeate enriched in carbon dioxide to be flared or reinjected into the ground. Currently, cellulose acetate is the most widely used membrane material for this separation, but because the carbon dioxide/methane selectivity of cellulose acetate is only 15–20, two-stage systems are often required to achieve a sufficient separation. More selective polyimide membranes are beginning to replace cellulose acetate membranes in this application. Flow schemes for a one-stage (A) and a two-stage (B) cellulose acetate membrane system for carbon dioxide/natural gas separations are shown in **Figure 17**. The single-stage system has a low capital cost, but 12.7% of the methane in the gas is lost with the carbon dioxide. This loss becomes unacceptable for large systems, so a two-stage unit is used. The methane loss is reduced to less than 2% but at the expense of more membrane area and a large compressor. The membrane process is generally best suited to relatively small streams in the 5–20 MMscfd range, but the economics of the process have slowly improved over

Table 2 Membrane gas separation applications

Separation	*Status*
H_2/N_2, CO, CH_4, etc.	~500 units installed. Various hydrogen recovery applications in refineries, petrochemical and ammonia plants
CO_2/CH_4	~200 units installed, some very large (5000–50 000 scfm) to separate carbon dioxide from natural gas
N_2/air	~5000 units installed, most small in the 50–500 scfm range (98–99.5% nitrogen)
Organic solvent vapour/air, N_2	~100 units installed. Diverse applications include gasoline vapour recovery at oil terminals, recovery of monomers from reactor vents
H_2O/air	Many thousands of small modules sold for drying compressed air

the years and more than 200 natural gas treatment plants have now been installed – some quite large.

By far the largest gas separation process in current use is the production of nitrogen from air. The first membranes used for this process were based on polysulfone, poly(trimethylpentane) and ethyl cellulose. These polymer materials had oxygen/nitrogen selectivities of 4 to 5, and the economics of the process were marginal. The second-generation materials now used have selectivities in the range 6 to 7. With these membranes, the economics of nitrogen production from air are very favourable, especially for small plants producing 50–500 scfm of nitrogen; 5000 of these small systems are now in operation. In this range, membranes are the low-cost process, and most new nitrogen plants use membrane systems.

A growing application of membrane systems is the removal of condensable organic vapours from air and other streams. Unlike the process described above, organic vapour separation uses rubbery membranes, which are more permeable to the organic vapour. More than 100 organic vapour recovery plants have been installed. In Europe, most of the plants recover gasoline vapours from air vented during transfer operations; in the USA, most plants recover chlorinated and fluorinated hydrocarbons from refrigeration or chemical processing streams. Separation of propylene from nitrogen in polyolefin plants is an emerging application worldwide.

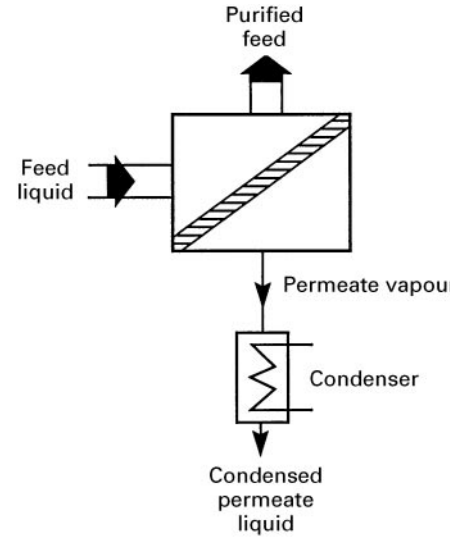

Figure 18 In the pervaporation process, a liquid contacts the membrane, which preferentially permeates one of the liquid components as a vapour. The vapour, enriched in the more permeable component, is cooled and condensed, spontaneously generating a vacuum that drives the process.

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Pervaporation

The process Pervaporation is a membrane process used to separate liquid mixtures. The feed liquid contacts one side of a membrane, which selectively permeates one of the feed components, as shown in **Figure 18**. The permeate, enriched in this component, is removed as a vapour from the other side of the membrane. The driving force for the process is the low vapour pressure on the permeate side of the membrane, which is generated by cooling and condensing the permeate vapour. The separation achieved is proportional to the differences in rates of permeation of the components of the mixture through the membrane.

Pervaporation offers the possibility of separating solutions, mixtures of components with close boiling points, or azeotropes that are difficult to separate by distillation or other means. An illustration of the ability of pervaporation membranes to break azeotropes is shown in **Figure 19** for the separation of benzene/cyclohexane mixtures. The vapour–liquid equilibrium for the mixture shows that benzene/cyclohexane mixtures form an azeotrope at approximately 50% benzene. Distillation is unable to separate a feed stream of this composition. However, pervaporation treatment of this mixture produces a vapour permeate containing more than 95% benzene.

The first systematic work on pervaporation was done by Binning and co-workers at American Oil in the 1950s. The process was not commercialized at that time and remained a mild academic curiosity until 1982, when GFT (Gesellschaft für Trenntechnik

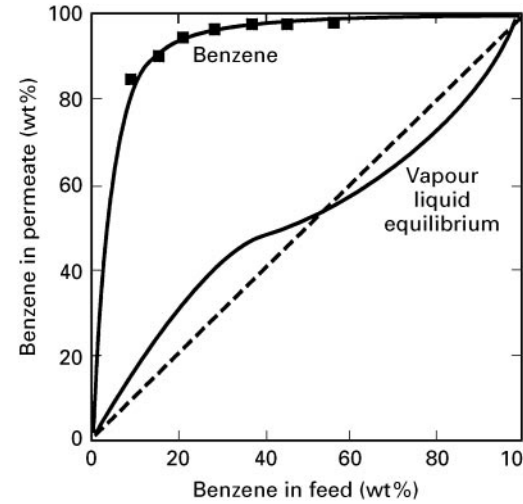

Figure 19 Fraction of benzene in permeate as a function of feed mixture composition for pervaporation at the reflux temperature of a binary benzene/cyclohexane mixture. (Reprinted with permission from *Industrial and Engineering Chemical Research* 22 (1983) 313. Copyright 1983 American Chemical Society.)

GmbH, Germany) installed the first commercial pervaporation plant. That plant separated water from concentrated alcohol solutions; GFT has since installed more than 50 such plants. The ethanol feed to the membrane generally contains ~10% water. The pervaporation process removes the water as the permeate, producing pure ethanol with less than 1% water, and avoiding all the problems of azeotropic distillation.

Spurred on by this success, a great deal of effort is being made to apply pervaporation to other difficult separations. Exxon, for example, pursued the separation of hydrocarbon mixtures containing aromatics and aliphatics, a major separation problem in refineries. Another application is the separation of dissolved volatile organic compounds (VOCs) from water, developed by Membrane Technology and Research, Inc.

Applications To date, the largest application of pervaporation is the dehydration of ethanol or isopropanol. This process has been pioneered by GFT, now a division of Sulzar, using polyvinyl alcohol composite membranes that are far more permeable to water than alcohol. A flow scheme of a GFT plant combining distillation and pervaporation to produce dry alcohol is shown in **Figure 20**. The distillation column produces an ethanol overhead stream containing 85–90% ethanol which is fed to the pervaporation system. To maximize the vapour pressure driving force across the membrane the pervaporation module usually operates at a temperature of 105–130°C, corresponding to a need stream vapour pressure of 2–6 atm. The permeate vapour is cooled and condensed at 0 to −10°C. The permeate contains 40–50% ethanol which is recycled to the distillation column; the residue stream is better than 99.5 wt% ethanol. Most of the installed solvent dehydration systems have been for ethanol dehydration, but applications to other solvents, including isopropanol, glycols, acetone and methylene chloride, have also been studied.

The only other commercial pervaporation application is the separation of dissolved VOCs from water. Relatively hydrophobic composite membranes, such as silicone rubber coated on a microporous polyimide support membrane, are used. Extremely high separation factors can be obtained for the more hydrophobic VOCs such as toluene, benzene, chlorinated solvents, esters and ethers. Frequently the VOC in the condensed permeate is enriched 100- to 1000-fold over the feed. Target applications include removal of VOCs from industrial wastewater streams and the recovery of volatile flavour and aroma components in the food processing industry. The GC traces in **Figure 21** illustrate the concentration and recovery of orange juice flavours from the water evaporated from orange juice obtained by pervaporation.

The current commercial pervaporation processes involve the separation of organics and water. This separation is relatively easy, because organic solvents and water have very different polarity and exhibit distinct membrane permeation properties. No commercial pervaporation systems have yet been developed for the separation of organic/organic mixtures. However, current technology now makes development of pervaporation for these applications possible, and the process is being actively developed by a number of companies. The first pilot-plant results for an organic–organic application – the separation of methanol from methyl *t*-butyl ether/isobutene mixtures – was reported by Separex in 1988. This is a particularly favourable application, and available cellulose acetate membranes achieve a good separation. More recently, Exxon started a pervaporation pilot plant for the separation of

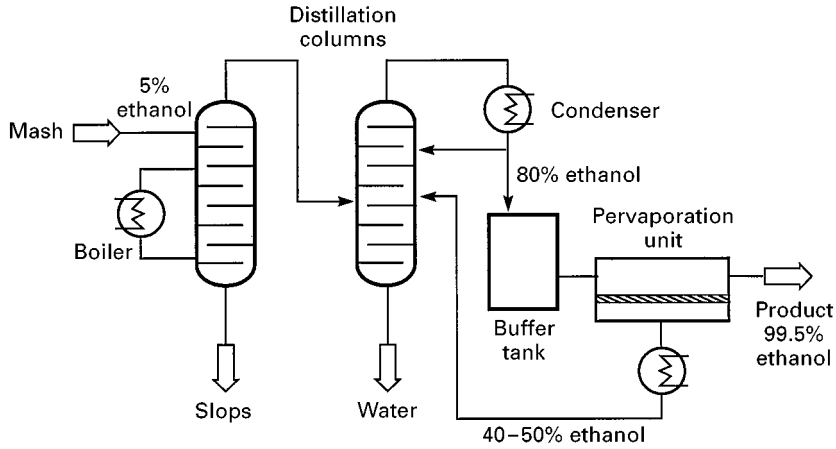

Figure 20 Flow scheme of an integrated distillation/pervaporation plant for ethanol recovery from fermentors.

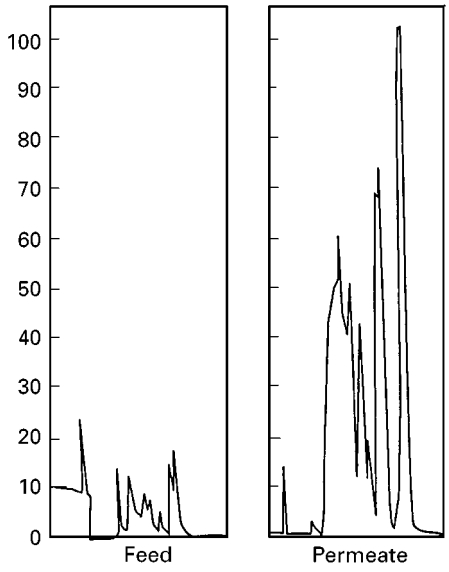

Figure 21 HPLC traces showing recovery of flavour and aroma components from orange juice evaporation condensate by pervaporation.

aromatic/aliphatic mixtures, using polyimide/polyurethane block copolymer membranes.

Dialysis

The process Dialysis was the first membrane process to be used on an industrial scale with the development of the Cerini dialyser in Italy. The production of rayon from cellulose expanded rapidly in the 1930s, and a need arose to recover sodium hydroxide from hemicellulose/sodium hydroxide solution by-product streams formed in the process. A finely microporous membrane was used to separate the concentrated hemicellulose solution from water. The smaller sodium hydroxide molecules diffuse across the membrane down a concentration gradient to produce an uncontaminated product stream, as shown in **Figure 22**.

With the development of ultrafiltration and microfiltration membranes in the 1960s and 1970s, industrial applications of dialysis largely disappeared because dialysis membranes were slow and unselective compared to the newer technologies. However, in the medical area, two very large applications have been developed, namely the dialysis of blood – haemodialysis – in the artificial kidney, and the related process used to exchange oxygen and carbon dioxide in blood in the artificial lung. Both processes use the low-pressure, mild conditions of dialysis.

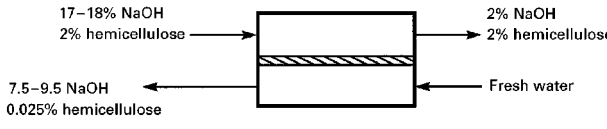

Figure 22 The separation of sodium hydroxide from hemicellulose by dialysis. This separation became important in the production of rayon in the 1930s and 1940s.

Applications

Haemodialysis (artificial kidney) The kidney is a key component in the body's waste disposal and acid–base regulation mechanism. Approximately 1 in every 10 000 persons will suffer irreversible kidney failure, which before 1960 was invariably fatal. Now a number of treatments, of which haemodialysis is by far the most important, can maintain these patients. As many as 800 000 patients worldwide are treated by haemodialysis devices. Each patient is dialysed two to three times per week with a dialyser that contains about one square metre of membrane area. Economies of scale allow the membrane modules to be produced at about US$15 each. The devices are generally disposed of after one or two uses. As a result the market is about US$1.3 $\times 10^9$ per year, making this the largest membrane separation process in terms of sales per year and membrane area used.

The first successful artificial kidney was constructed by Kolf and Berk in Holland in 1945. Over the next 20 years Kolf and others developed a number of improved devices, and by the 1960s the process began to be widely used. Early dialysers used coiled tubes or plate-and-frame designs. The development of hollow-fibre dialysers reduced costs considerably, making widespread use of the process possible. Each fibre dialyser contains 0.5–2.0 m^2 of membrane formed as fibres 0.1–0.2 mm in diameter. A typical dialyser module (**Figure 23**) contains several thousand fibres in a 2 in (5 cm) diameter tube 1–2 ft (30–60 cm) long. Blood flows down the bore of the fibre, and an isotonic saline solution is circulated around the outside. Urea, creatinin and other metabolites in the blood diffuse through the membrane to the dialysate solution. The process must be carried out

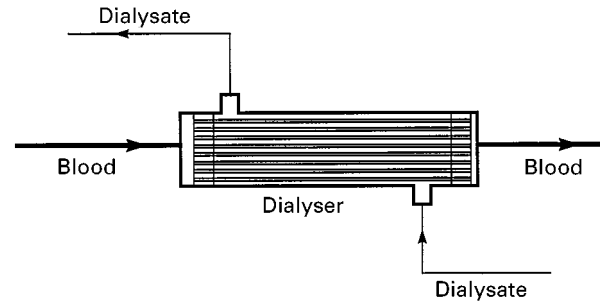

Figure 23 Schematic of a hollow-fibre haemodialyser.

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slowly to avoid shock to the patient; typically 2–4 h are required to eliminate all of the accumulated toxins.

Blood oxygenators (artificial lungs) Blood oxygenators are used during heart surgery. Until the early 1980s direct oxygenation of blood was used to maintain patients during surgery. Rotating discs or small countercurrent contacting towers delivered oxygen to the blood and removed carbon dioxide. This procedure required a large volume of blood to prime the units and damaged the blood during long surgeries. The introduction of hollow-fibre membrane contactors largely solved both of these problems and was one reason for the dramatic expansion of open-heart surgery in the 1980s. Currently, about one million procedures are performed annually world-wide. A successful heart-lung must normally deliver about 250 cm^3(STP) per min of oxygen and remove about 200 cm^3(STP) per min of carbon dioxide. Microporous polyolefin hollow-fibre membrane modules with a membrane area of 2–10 m^2 are generally used.

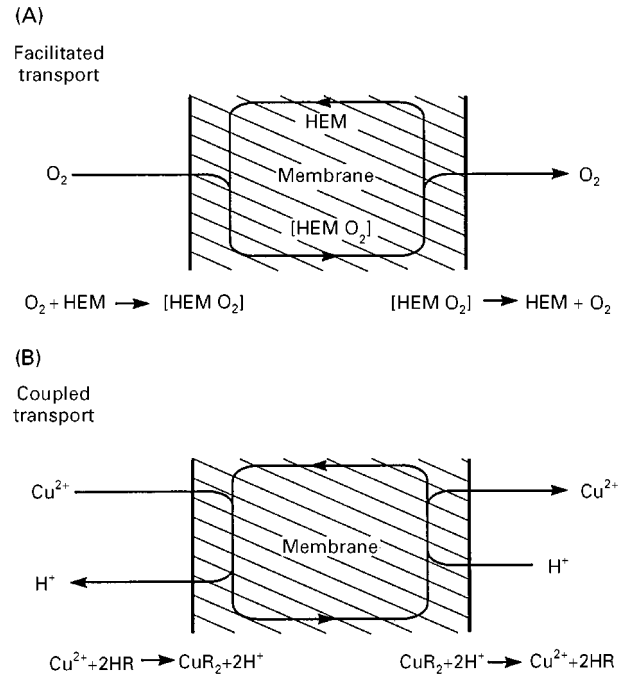

Figure 24 Schematic examples of (A) facilitated and (B) coupled transport of gas and ions. The facilitated transport example shows the transport of oxygen across a membrane using haemoglobin as the carrier. The coupled transport example shows the transport of copper ions across the membrane using a liquid ion exchange reagent as the carrier.

Other Membrane Separation Processes

The seven processes described above represent the majority of commercial membrane separation technologies. However, a number of processes are still in the laboratory or early commercial stage and may yet become important. These processes are described briefly below.

Carrier-Assisted Transport

Carrier-assisted transport usually employs liquid membranes containing a complexing or carrier agent. The carrier agent reacts with one permeating component on the feed side of the membrane and then diffuses across the membrane to release the permeant on the product side of the membrane. The carrier agent is then reformed and diffuses back to the feed side of the membrane. Thus, the carrier agent acts as a shuttle to transport selectively one component from the feed to the product side of the membrane.

Facilitated transport membranes can be used to separate gases; membrane transport is then driven by a difference in the gas partial pressure across the membrane. In the example shown in **Figure 24**, the carrier is haemoglobin, used to transport oxygen. On the upstream side of the membrane, haemoglobin reacts with oxygen to form oxyhaemoglobin, which then diffuses to the downstream membrane interface. There, the reaction is reversed – oxygen is liberated to the permeate gas and haemoglobin is reformed. The haemoglobin then diffuses back to the feed side of the membrane to pick up more oxygen. In this process haemoglobin acts as the shuttle, transporting oxygen selectively through the membrane. Other gases, such as nitrogen, which do not react with the carrier, are left behind.

Coupled transport is similar to facilitated transport and also incorporates a carrier agent in the membrane. However, in coupled transport the carrier agent couples the flow of two species. Because of this coupling, one of the species can be moved against its concentration gradient, provided the concentration gradient of the second coupled species is sufficiently large. In the example shown in Figure 24, the carrier is an oxime that forms an organic-soluble complex with copper ions. The reaction is reversed by hydrogen ions. On the feed side of the membrane, two oxime carrier molecules pick up a copper ion, liberating two hydrogen ions to the feed solution. The copper–oxime complex then diffuses to the downstream membrane interface, where the reaction is reversed because of the higher concentration of hydrogen ions in the permeate solution. The copper ion is liberated to the permeate solution and two

hydrogen ions are picked up. The reformed oxime molecules diffuse back to the feed side of the membrane. Metal ions can also be selectively transported across a membrane, driven by a flow of hydrogen or hydroxyl ions in the other direction.

Because the facilitated and active transport processes employ a reactive carrier species, very high membrane selectivities can be achieved – often far larger than those achieved by other membrane processes. This has maintained interest in facilitated transport since the 1980s, yet no significant commercial applications exist or are likely to exist in the immediate future. The principal limitations are the physical instability of the liquid membrane and the chemical instability of the carrier agent.

Membrane Reactors

In membrane reactors, the membrane is used to shift a chemical equilibrium or separate the products of a reaction. A wide variety of processes have been suggested, and a few have reached the commercial stage. A simple example is shown in **Figure 25** – the reaction of *n*-butane to butadiene and hydrogen: $C_4H_{10} \rightleftharpoons C_4H_6 + 2H_2$.

This is an equilibrium reaction and in a conventional process a mixture of components is withdrawn from the reactor, separated, and the unreacted *n*-butane recirculated to the feed. In the membrane reactor, hydrogen is removed through the membrane so that the chemical equilibrium in the reactor is shifted to the right and the conversion of *n*-butane to butadiene is increased. Essentially pure butadiene leaves the reactor. This type of process is the subject of a considerable research effort, mostly using ceramic membranes operating at high temperatures. The development of these devices for the production of syngas (a mixture of carbon monoxide and hydrogen) is the focus of very large research programmes at Air Products and Standard Oil. Promising results have been obtained in the laboratory, but scale-up to an economical process is still far off.

Membrane Contactors

In the membrane separation processes discussed so far, the membrane acts as a selective barrier allowing relatively free passage of one component while retaining another. In membrane contactors the membrane function is to provide an interface between two phases but not to control the rate of passage of permeants across the membrane. An example of this technology, in which the membrane is used in a process to deoxygenate water, is shown in **Figure 26**.

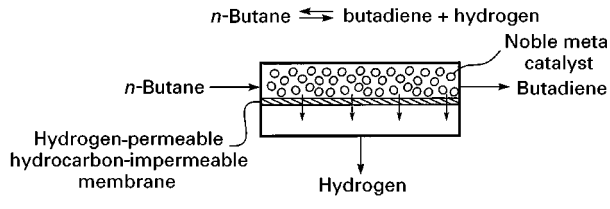

Figure 25 Schematic of a membrane reactor to separate butadiene from *n*-butane.

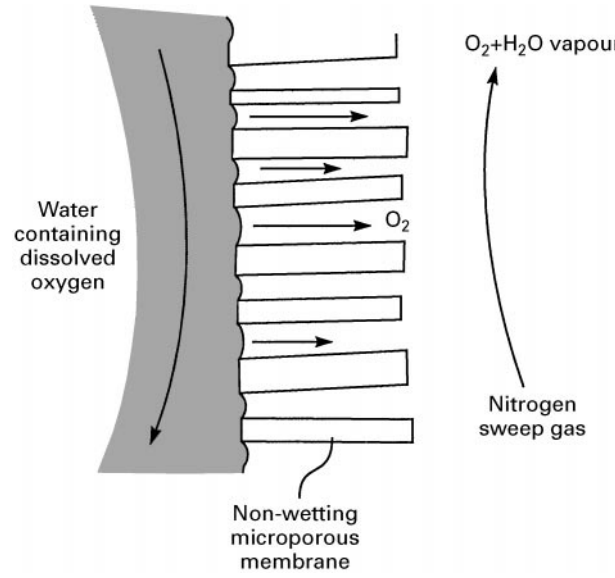

Figure 26 Schematic showing application of a membrane contactor to remove dissolved oxygen from water. This process is used to prepare power plant boiler feed water.

A hollow-fibre microporous membrane separates the oxygen-containing water from the nitrogen sweep gas. Even though the dissolved oxygen concentration in the water is very low, its equilibrium concentration in the gas phase in contact with the water is several thousand times higher. This means that oxygen permeation through the membrane down the concentration gradient to the nitrogen sweep gas is high. The membrane provides a large surface contact area between the water and nitrogen sweep gas but does not affect the relative permeabilities of oxygen and water vapour through the membrane. In this type of application, the membrane serves as a contactor or phase separator. Exactly the same separation could be achieved by running the water and nitrogen countercurrent to each other in a packed tower, but membrane contactors are much more compact. Membrane contactors are typically shell- and tube-devices containing microporous capillary hollow-fibre membranes. The membrane pores are made sufficiently small that capillary forces prevent direct mixing of the two phases on either side of the membrane.

A small market has already developed for membrane contactors to degas ultrapure water for the electronics industry and boiler feed water for power

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plants. The long-term goal of the process is to replace packed towers in conventional absorber–stripper operations. Practical problems related to membrane fouling and lifetime are the principal limitations.

The Future

Since the 1970s there has been a period of very rapid growth for the membrane separation industry. Total sales for all membrane applications have grown approximately 400-fold to the US$3–4 $\times 10^9$ per year level. In the areas of microfiltration, ultrafiltration, reverse osmosis, electrodialysis and dialysis, the technology is relatively mature. Significant growth is still occurring, however, as membranes continue to displace more conventional separation techniques. The most rapidly expanding area is gas separation, which has grown to a US$150 $\times 10^6$ per year business in just a few years. Gas separation is poised to grow a further two- or three-fold as the technology is used more widely in the refinery, petrochemical and natural gas processing areas. If the development of ceramic oxygen-permeable membranes for syngas membrane reactors is successful, a membrane process that could change the basis of the chemical industry would then be available.

Further Reading

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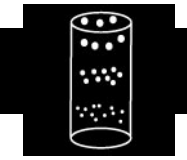
PARTICLE SIZE SEPARATIONS



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Historical Development

In 1556, an extraordinary book entitled *De Re Metallica*, *Libri XII* appeared in Basel. The author was a German physician, naturalist and mineralogist, calling himself Georgius Agricola (originally called Georg Bauer), living in Jáchymov, Bohemia, from 1494 to 1555. Agricola described, in a fascinating manner, the contemporary advances in metals and minerals recovery and gave us a very detailed report on the sophisticated technologies of his epoch. This late medieval period saw a true expansion of science and technology in Europe. Winston Churchill once said: '… from this date, 1492, a new era in the history of mankind takes its beginning'. As many metal recovery processes used at that time were based on various separations of particulate matter and *De Re Metallica*, *Libri XII* seems to be the first printed review of separation technologies, it is fitting to acknowledge Agricola's publication priority in this field and to consider his book as the beginning of a modern scientific approach to particle size separations.

The reproduction of a rendering in **Figure 1** taken from Agricola's book shows a surprisingly sophisticated device for gold (and other metals) recovery by 'panning' or 'sluicing' which used gravity and

[1] This article does not deal with the important particle separation techniques of filtration, flotation and the use of membranes which are dealt with elsewhere in the Encyclopedia.